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TREATMENT OF GASES

Abstract:

Abstract of GB1382984

1382984 Treating exhaust gas IMPERIAL CHEMICAL INDUSTRIES Ltd 12 April 1972 [20 April 1971] 10034/71 Heading F1B A method for reducing the quantity of carbon monoxide, hydrocarbons or nitrogen oxides in gases which comprises contacting the said gases under substantially non-oxidizing conditions i.e. the oxygen content of the gases is less than the equivalent of the oxidizable materials present in the gases with a fibrous catalyst comprising a synthetic refractory fibre and a catalytic agent which promotes one or more reactions by which at least one of the said components is wholly or partly destroyed. The fibrous catalyst is prepared by fibrizing an aqueous solution of alumina and/or zirconium and a water-soluble organic polymer, preferably partially hydrolyzed polyvinyl acetate, drying the fibre and heating to decompose the organic polymer and the aluminium or zirconium salt to form a fibre comprising the oxides of the metals. The fibres may include additives such as:- grain growth inhibitors e.g. magnesium or calcium salts; phase change stabilizers, e.g. salts of yttrium or the rare earths, calcium oxide or zirconia; reinforcing particles e.g. colloidal silica; or compounds which improve the refractory qualities of the fibres e.g. acid oxides. The average diameter of the fibres is less than 20 microns e.g. 0.5 to 14.8 microns. Their thermal conductivity is less than 0.02 e.g. 0.0001 to 0.01 calories per second per degree C per centimetre cube. Their surface area is greater than 0.5 sq. m/gm. preferably 5 to 150 sq. m/gm. The catalytic agents include Group VIII metals of the Periodic Table, especially ruthenium, iridium, rhodium, nickel or cobalt, singly or in mixtures, and may be present as elementary metal in finely-divided form or as an oxide. When the fuel producing the gases contains a considerable quantity of sulphur (200 to 1,000 ppm, w/w) a first stage of the catalyst is preferably cobalt, suitably cobalt oxide. The gases contact the catalyst at a temperature of at least 400 C, preferably 600 C to 1000 C. When an engine which produces the gases is being started-up, oxidizing air is initially added to the gases until the fibrous catalyst reaches its working temperature. A second stage of the catalyst comprises an oxidation stage and/or further reaction over a carbon monoxide shift or methanation catalyst. The synthetic refractory fibre is an inorganic oxide of alumina, zirconia, titania or silica. The proportion of catalytic agent in the fibrous catalyst is 0.001 to 1.0 wt. per cent in the case of ruthenium, iridium or rhodium and 1.0 to 10.0 wt. per cent in the case of nickel or cobalt. The oxidation stage is carried out using a platinum group metal in a concentration of 0.002 to 1.0% on a refractory support. Alternatively the oxidation catalyst is an oxide of one or more base metals from Group VIII of the periodic table or an oxide of chromium or tungsten. Some of the exhaust gas may be recycled to the engine inlet. Data supplied from the esp@cenet database - Worldwide

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(54) TREATMENT OF GASES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of gases, especially the treatment of gases to diminish the quantity of pollutant gases contained therein.

Waste gases frequently contain varying proportions of gaseous components which cause pollution problems when they are discharged to atmosphere. For example, gases resulting from the combustion of hydrocarbons contain carbon monoxide, unburnt hydrocarbons and nitrogen oxides, and the pollution problem is especially serious in the case of exhaust gases from internal combustion engines. Waste gases from nitric acid plants also contain nitrogen oxides. Means for reducing the content of polluting gases in waste gases is clearly very desirable.

Legislation introduced in the USA has prescribed upper limits for the allowable levels of hydrocarbons, carbon monoxide and oxides of nitrogen in automobile exhaust gases. The desirability of treating exhaust gases catalytically has been recognised for many years but prior processes have not provided a catalytic treatment which reduces all the pollutants simultaneously to desirably low values for sufficiently long periods of use.

Most of the prior processes for the catalytic treatment of vehicle exhaust gases have involved the addition of air to the gases. There have been proposals (US Patents 3,370,914, 3,493,325, 3,228,746 and 3,544,264) to treat exhaust gases in the absence of secondary air, but these proposals have not apparently found general application.

The catalysts are generally used on refractory supports and, for exhaust gas treatment processes involving high temperature after-

burning (i.e. oxidation) techniques, the use of asbestos and metal fibres has been proposed (US Patents 1,875,024 and 3,495,950).

According to our invention we provide a method for reducing the quantity of the components carbon monoxide, hydrocarbons or nitrogen oxides in gases which comprises contacting the said gases under substantially non-oxidising conditions with a fibrous catalyst comprising a synthetic refractory fibre and a catalytic agent which promotes one or more reactions by which at least one of the said components is wholly or partly destroyed.

By substantially non-oxidising conditions, it is meant that the content of oxygen in the gases is less than the equivalent of the oxidisable materials present in the gases. Preferably the oxygen content of the gases is less than half the said equivalent.

Preferably, the catalytic agent is one which promotes more than one (and, if possible, all) of the said reactions. In its simplest form, the method of the invention comprises contacting the gases with a single fibrous catalyst, but if desired the gases may be contacted in two or more stages or with a mixed fibrous catalyst. Multiple contacting may, for example, be such as to bring the gases in contact with the same fibrous catalyst repeatedly, or to bring the gases into contact with different fibrous catalysts in succession, or to enable the contact to be carried out under different conditions (for example at different temperatures or contact times), or any combination of these.

The gases are contacted with the catalyst at a temperature sufficient to ensure that the catalyst functions effectively. For the decomposition of hydrocarbons and nitrogen oxides the temperature is preferably above 400° C., especially above 600° C. and up to about 1000° C. It is preferred that steps be taken to ensure that the fibrous catalyst reaches its active temperature as soon as possible when in use and is maintained at such a temperature during use. It is usually most convenient to maintain the desired temperature by thermal

insulation of the catalyst container or by using the sensible heat of the waste gases especially in the case of those produced by a combustion process, but if desired this heat can be modified by supplementary heating or cooling of the catalyst in its container. It is therefore especially convenient to site the catalyst as near as practicable to the combustion zone in which the gases are produced, for example close to the exhaust outlet of an internal combustion engine. Alternatively the catalyst may be heated by combustion using an auxiliary air supply, which can be used during warm-up, that is when the engine and catalyst are below working temperature, but thereafter cut off, for example by a mechanism known for effecting automatic cold-start carburettor adjustment or equivalent mechanism.

Thus this form of the invention may be defined as a method for treating an internal combustion engine exhaust gas having a prior start-up phase and a running phase, the start-up phase being operated under oxidising conditions with added air in the presence of the fibrous catalyst until the normal operating temperature of that catalyst has been reached, and the running phase being operated thereafter under non-oxidising conditions. If the non-oxidising reaction over the fibrous catalyst is followed by an oxidation stage as herein-after described, this form of the invention may be operated by having an air supply upstream of the fibrous catalyst during the start-up phase and between the fibrous catalyst and the oxidation catalyst during the running phase. The start-up phase may be extended until the catalyst of any subsequent stage has been heated to its operating temperature.

The quantity of air supplied in the said start-up phase need not be sufficient to afford over-all net oxidising conditions, provided there is sufficient to produce exothermic reaction. The air supply may usefully be preheated, especially for the start-up phase.

The fibrous catalyst may comprise any catalytic agent active for the reaction concerned and this active agent may be distributed throughout the refractory fibre or may be concentrated locally therein for example as a surface coating or in the surface zones of the fibre. The refractory fibre may be inert or may usefully have some catalytic activity for any of the reactions, or it may enhance the catalytic activity of the catalytic agent.

The fibrous catalyst may be associated with an inorganic fibre used for example as an inert diluent or as a support or reinforcing material. Suitable fibres for this purpose include any of the refractory fibres used to make the fibrous catalyst and natural or artificial fibres such as asbestos, mineral wool and the like.

Especially suitable fibrous catalysts are those derived from aluminium phosphate fibres as are more fully described in U.K. Patent Specification No. 1,322,725, carbon fibre or fibres

of the carbides of, for example, titanium, silicon, boron or zirconium. More especially suitable are fibrous catalysts derived from refractory inorganic fibrous oxides, for example fibres of alumina, zirconia, titania or silica. Fibres comprising the said oxides in combination, either physically or chemically may also be used.

We especially prefer to use fibrous catalysts derived from refractory fibres prepared as disclosed in U.K. patent specification No. 1,360,197. These disclosures are incorporated herein by reference.

As disclosed in the aforesaid specification, especially useful fibrous catalysts comprise a catalyst material and an alumina and/or zirconia fibre prepared by fibrising a composition having a viscosity greater than 1 poise comprising an aqueous solution of a salt of alumina and/or zirconium (as the case may be) and a water-soluble organic polymer, preferably partially-hydrolysed polyvinyl acetate, drying the fibre thereby formed, and heating to decompose the organic polymer and the aluminium or zirconium salt to form a fibre comprising the oxides of the metals. Preferred salts of aluminium or zirconium are the acetates, nitrates, sulphates or oxychlorides. Fibrising of the composition is most effectively carried out by a blowing process, especially when mats or felts of fibrous catalysts are required.

Fibrous catalysts derived from alumina or zirconia may advantageously contain various additives, conveniently included in the fibre by adding them to the fibrising composition. Examples of additives which may be included are:

- (a) grain growth inhibitors, for example salts of magnesium or calcium,
- (b) phase-change stabilizers, for example salts of yttrium or the rare earths; calcium oxide or zirconia,
- (c) reinforcing particles such as colloidal silica,
- (d) compounds which improve the refractory qualities of the fibre, for example acid oxides (especially SiO_2 , B_2O_3 , P_2O_5 or ZrO_2 in the case of alumina fibre).

The average diameter of fibres from which fibrous catalysts for use in the invention are made is preferably less than 20 microns, for example in the range 0.5 to 5 microns. The thermal conductivity of the material of the fibre is preferably less than 0.02, for example in the range 0.0001 to 0.01 calories per second per degree C per centimetre cube. The surface area of the fibrous catalyst is preferably greater than 0.5 square metres per gram, more preferably from 5 to 150 square metres per gram.

The catalytic agents which may be used, especially for the processes carried out at above 400° C., include metals of Group VIII of the

Periodic Table or mixtures thereof, and especially ruthenium, iridium, rhodium, nickel or cobalt. The metals may be present in the form of the elementary metal (in which case it is preferably in a finely-divided form) or as a compound of suitable activity, for example an oxide. If desired, the metal may be initially in the form of a salt or other derivative which is convertible into the active catalytic form by a treatment prior to use (for example by heating, oxidising, or reducing) or under the conditions of use for treating the waste gases. When the active metal is cobalt the process of the invention is especially suitable for treating the exhaust from an internal combustion engine consuming a fuel containing sulphur compounds. We have discovered that, whereas nickel is poisoned by sulphur both for the hydrocarbon/steam reforming reaction and for reactions which remove nitrogen oxides, cobalt is poisoned less for the hydrocarbon/steam reaction and very much less for nitrogen oxides removal. Thus, when the sulphur content of the gasoline fuel fed to the engine is considerable, for example 200 to 1000 ppm w/w as sulphur, the active metal of the first stage catalyst preferably is cobalt. However since the quantity of cobalt catalyst required is greater the greater the sulphur content, this form of the invention is most economical and effective at lower sulphate contents, for example up to 250 ppm w/w as sulphur, such as can be supplied by gasoline manufacturers without an excessive price increase.

If a cobalt catalyst is used, it is very suitable of the type consisting essentially (over 70%) of cobalt oxide Co_3O_4 , since in general cobalt is less catalytically-active than nickel.

At temperatures of above 600°C ., using some catalysts, notably nickel, cobalt, copper or iron, hydrocarbons are largely removed by reaction with steam and any residual oxygen; nitrogen oxides are removed by reduction; and ammonia formed by such reduction is cracked to nitrogen and hydrogen. The conditions of temperature, catalytic activity and space velocity are chosen preferably so that at least 70% of the nitrogen oxides are destroyed, but at most 20% thereof is converted to ammonia; without the use of excessive temperature or large catalyst volume, over 90% destruction with under 10% ammonia formation is possible. These reactions take place more efficiently the higher the temperature. The effluent from this process can, if desired, be made innocuous by oxidation using known methods or by further reaction over a carbon monoxide shift or methanation catalyst. A carbon monoxide shift catalyst is a catalyst which will promote the reaction of carbon monoxide and steam to give carbon dioxide and hydrogen. A methanation catalyst is a catalyst which will promote the reduction of carbon monoxide by

hydrogen to form methane. For hydrocarbon removal and shift reaction it is necessary to ensure the presence of a sufficient quantity of steam in the gases.

As an alternative the process may be carried out at a temperature in the range 400 – 600°C ., at which temperatures extensive reaction of carbon monoxide with steam takes place, nitrogen oxides are largely converted to ammonia which is not decomposed, and partial reaction of hydrocarbons with steam takes place. However, by using certain catalysts, notably ruthenium, iridium or rhodium, at these temperatures little ammonia is formed. The effluent from such processes can be made innocuous by oxidation, for example by contact with a suitable catalyst such as nickel molybdate.

The fibrous catalyst may be used in the shift reaction or methanation reaction. For the shift reaction the temperature may be 350 – 550°C . over a catalyst of the "high-temperature" type (for example nickel, zinc oxide/chromia, cobalt molybdate or iron oxide/chromia) or 150 – 300°C . over a catalyst of the "low-temperature" type (for example copper with an oxide of zinc and/or manganese, chromium, magnesium or aluminium). For the methanation reaction (temperature 200 – 350°C .) a nickel or cobalt catalyst is most suitable. The shift and methanation catalysts can be made in the same way as the catalysts for use at higher temperatures.

If a low-temperature shift catalyst is used it may be protected from sulphur by a guard bed suitably of zinc oxide, iron oxide or cobalt oxide; and if halogen is likely to be present in the exhaust gases, a guard-bed containing a material more basic than zinc oxide is preferably used. A catalyst comprising a combination or mixture of high-temperature and low-temperature shift catalysts is also very effective. Which shift stage is used will depend on the composition of outlet gas required and on the sulphur content of the gas, the high temperature type being favoured if the available fuel contains sulphur to the extent of more than 50 ppm w/w.

For oxidation of vehicle exhaust gases after treatment by the process of the invention, inlet temperatures of 200°C . to 600°C . are suitable but temperatures above 600°C . can be used, in which event little if any cooling is required. In steady running the air ejected between the fibrous catalyst and the oxidation stage should be at a rate sufficient to oxidise the carbon monoxide and hydrocarbons and afford a moderate excess for example up to 2% v/v. Suitably 2–3% v/v of oxygen is added in steady running conditions, but appropriately more in cold-starting or in coasting, since more hydrocarbon and carbon monoxide are present.

If the hydrocarbon or nitrogen oxides removal is followed by an oxidation, the oxida-

tion catalyst is preferably a precious metal from Group VIII of the Periodic Table (according to Sidgwick "The Chemical Elements and their Compounds, Oxford 1950); this is in particulate form or on a mechanical support such as a monolithic refractory or fibrous or woven metal wire structure. Conveniently the oxidation catalyst is a cobalt catalyst of the type which may be used for the hydrocarbon or nitrogen oxides removal or a suitably promoted supported cobalt catalyst such as a copper-cobalt catalyst. Others which can be used include copper chromite and also platinum group metals, especially palladium, alone or together with one or more base-metal promoters such as copper or its oxides, preferably on a refractory support such as anhydrous alumina. The concentration of the platinum group metal is suitably in the range 0.002 to 1.0%, calculated as metal.

A very suitable oxidation catalyst comprises the oxide of one or more base metals from Group VIII of the Periodic Table and an oxide of chromium or tungsten, preferably in intimate association. This catalyst contains the two oxides preferably in a proportion between half and double that which exists in the chromates or tungstates, conveniently in about equi-atomic proportions with respect to the metals.

The oxides are preferably brought together by co-precipitation, especially of the Group VIII metal cation with a chromate or tungstate, followed by heating to decompose the chromate or tungstate to a lower oxide. The catalyst may contain support materials such as alumina, silica or magnesia.

The proportion of catalytically-active material in the fibrous catalyst depends on which reaction is to be catalysed and on which active material is to be used and is generally within the range 0.001–10% by weight. Thus for example platinum group metals show adequate activity for the hydrocarbon/steam reaction at lower concentrations—say 0.01 to 1% w/w as metal—than other metals of Group VIII of the Periodic Table, for example, nickel, for which about 2–10% (calculated as NiO) would be required to exert the same activity. Preferred concentrations of platinum group metals, for example ruthenium, iridium or rhodium, are 0.001 to 1% by weight calculated as metal. Preferred concentrations of cobalt or nickel are 1–10% by weight calculated as equivalent NiO. The proportion of catalytically-active material should of course be low enough not to impair the mechanical properties of the fibre.

Catalyst promoters may, in some embodiments, be included in the fibrous catalyst, for example alkali or alkaline-earth metal oxides (notably barium oxide for nickel), rare earth oxides or transition metal oxides.

The catalytic agent may be incorporated in the refractory fibre by coating or impregna-

tion techniques or by inclusion in the precursor from which the fibre is made, for example as described in U.K. patent specification No. 1,360,197.

It is convenient, especially in the case of fibrous catalyst derived from alumina or zirconia prepared according to U.K. patent specification No. 1,360,197, to disperse the catalytic agent in the composition which is fibrised. It is especially convenient when the catalytic agent, or its precursor can be dissolved in the said composition, for example water-soluble salts may be dissolved in aqueous solutions of aluminium or zirconium compounds suitable for fibrising.

Dispersion of the catalytic agent in the composition which is fibrised may also conveniently be carried out by mixing an insoluble or partly-soluble particulate catalytic agent with the fibrising composition. Preferably the mean size of particles thus dispersed should be smaller than the mean diameter of the fibre produced, and more particularly the particles should be colloidal size.

Any desired quantity of catalytic agent may be dispersed in the fibrising composition provided that the fibre formed is still sufficiently strong and coherent for use as a fibrous catalyst. We find that up to about 5% and in some cases up to about 10% by weight of a catalytic agent of suitable size may be incorporated in the fibre without serious deterioration in fibre properties.

It is preferred that the catalytic agent be chemically-compatible with the constituents of the fibrising composition. When the fibre is heated to form, for example, a refractory metal oxide, it is preferable for the catalytic agent to be stable at the temperature of heating. In the case of a catalytic agent precursor, it is frequently convenient for the catalyst to be formed from the said precursor during the heating of the fibre.

The catalytic agent may be incorporated into the fibre by soaking the fibre in a solution of the catalytic agent or its precursor in a suitable solvent and subsequently removing the said solvent from the fibre. Water is a suitable solvent for many catalytic agents or their precursors, for example metal salts. A fibre may be soaked before or after it is heated to form a fibre of different composition.

The catalytic agent may conveniently be deposited in a suitable form on at least part of the fibre surface. For this purpose it may, if desired, be bonded to the said surface by means of a binding agent, for example aluminium phosphate or alumina. Bonding may also be effected by means of an application of fibrising composition to the said surface or to the catalytic agent or both, and removal of the solvent of the said composition.

In embodiments in which no binder is used to assist adherence of the catalytic agent to

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the fibre surface, it is often possible to bring about some chemical interaction between the catalytic agent and the fibre to improve bonding. In most embodiments of the invention, however, it is satisfactory merely to deposit the catalytic agent on the fibre surface in a form sufficiently fine that the normal forces of physical attraction take effect. Thus it is convenient to deposit the catalytic agent from a mist or vapour comprising the catalytic agent or its precursor. Most conveniently the catalytic agent or its precursor is deposited on the fibre surface by treating the said surface with a dispersion comprising the catalytic agent or its precursor and a suitable liquid. A solution of the catalytic agent or its precursor in a volatile solvent is especially useful. In cases where the catalytic agent is dispersed in a liquid which does not dissolve it, it is preferred that the catalytic agent be in a finely-divided form, most preferably having a mean size less than 0.5 micron.

The fibrous catalyst may be treated, for example to bring about desired changes in the catalytic agent. For example, in cases where a catalytic agent precursor has been incorporated in or on the fibre, it will be necessary to generate the active catalytic agent by a suitable process. The processes normally used include chemical reaction to form a different compound, reduction and heating. Any of the processes, especially heating, may be combined with any desired step of heating the fibre to decompose, for example, metal compounds or the organic polymers in the fibrous composition. Treatment of the fibrous catalyst to achieve desirable physical changes in the catalytic agent may also be carried out; for example, changes in surface area or crystal structure may be desirable to achieve specific catalytic effects. Treatment of the fibrous catalyst to eliminate undesirable substances, for example catalyst poisons, may be useful in some embodiments.

The fibrous catalyst may be contained in a container of any convenient geometry and dimensions, and the container may contain the fibrous catalyst in one or more zones. The packing of the fibrous catalyst within the container may be adjusted to render the resistance to gas flow (the pressure drop) as low as may be desired. A packing density in the range 0.1 to 0.3 gm/cc is preferred. It is possible to use a wide range of container geometries, since the fibrous catalyst can readily adapt itself to fit almost any shape of container.

The invention thus provides in addition a reactor suitable for the process, comprising a chamber capable of holding the fibrous catalyst and means to conduct a stream of the gas into contact with the fibrous catalyst. The reactor may hold the catalyst in the form of loosely or partly compacted fibres or as

readily removable pre-formed shaped units. In the latter event the reactor preferably has at least one end-closure of such a size that a catalyst unit can be introduced or withdrawn bodily through it. The shaped units are conveniently contained in cages made of metal gauze or expanded metal.

It will be appreciated that the catalyst used in the process of the invention may exist at least partly in the reduced state and that then the gas-treatment vessels should for best results be air-tight and should be closed to the admission of air as soon as the flow of gas has ceased. In particular this may be effected by a non-return valve, at the outlet of the treatment system, and preferably distant from the catalyst, loaded or resiliently biased to close the outlet. For greater safety in this respect a second such valve may be disposed just downstream of the catalyst which it is to protect.

The use of fibrous catalyst has a number of advantages. Because of the small diameter of the fibre, mass transfer rates between the bulk gas phase and the active surface are very high compared with those for particulate catalysts. This means that highly-active catalysts can be utilised very effectively with consequential operation at high space velocities. This also means that the weight of catalyst required to produce a given conversion is likely to be smaller than necessary with conventional particulate catalysts. Also fibrous catalysts have shorter warm-up times. A suitable space velocity range is 30000 to 300000 hour⁻¹, and in certain cases we find that about one half to one-fifth of the weight of a conventional catalyst is required for the same result when using fibrous catalysts.

Owing to the strength of the fibres, which can be increased if they are felted, especially if an adhesive is present, the fibrous catalyst withstands vibration for long periods. This is important when the gases are derived from a reciprocating internal combustion engine, since the gases are delivered in pulses. The catalyst can conveniently be disposed in a reactor (such as the exhaust manifold or an extension thereof) rigidly fixed to the engine cylinder block, despite the vibration in the cylinder block.

The process of the invention are not, in general, strongly exothermic. Consequently self-heating of the catalyst, characteristic of reactions such as oxidation, does not take place. The fibrous catalyst, by reason of its low heat capacity and thermal conductivity, is thus especially suitable for processes taking place under substantially non-oxidising conditions.

The gases which may be treated by the method and devices of the present invention may be any gases containing carbon monoxide, hydrocarbons or nitrogen oxides. The

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5 treatment of exhaust gases produced by combustion, especially by combustion of hydrocarbons for example oil, natural gas and various petroleum products, including petrol, is particularly appropriate. The source of these gases may be any burner or combustion device which does not itself produce an adequately pure combustion gas, but the invention is especially suitable for the purification of the exhaust gases from internal combustion engines, most advantageously spark ignition engines.

10 The invention is thus applicable for example to the exhaust gases of reciprocating engines, rotary-piston engines and gas turbines and these engines may as fuel use, for example, town gas, natural gas, liquefied petroleum gas or liquid hydrocarbons such as gasoline, jet-fuel or diesel oil. Although, by maintaining temperatures in the higher part of the range for the primary stage and by guarding or not using a copper-based low temperature shift catalyst, fuels containing sulphur or halogen impurities can be used, it is preferred to use a fuel containing less than 200 ppm w/w of sulphur and substantially no halogen. Likewise, in order to maximise the active life of the catalysts, it is preferred to use gasoline of low lead content, for example, less than 0.4g of Pb per US gallon (3.8 litres), preferably under 0.01g, that is, substantially lead-free gasoline.

20 Since non-oxidising conditions are required for contact with the fibrous catalyst, it is preferable to operate the engines under rich-mixture conditions, such as produce an exhaust gas initially containing at least 1% of carbon monoxide. For a gasoline-fuelled engine this means that the air to fuel weight ratio is preferably not above 15.0 and is, for example, in the range 13 to 15.

25 An apparatus for the treatment of exhaust gases from an internal combustion engine by a method according to the invention is thus provided, which comprises an insulated first reactor adapted to be mounted close to an internal combustion engine and to be fed from the engine exhaust port or ports, a second reactor disposed downstream of the first reactor and an air inlet means adapted to feed alternatively at or before the insulated reactor and between the reactors.

30 The alternation of the air feed may be in response to an automatic start device, to catalyst temperature measurement or to a time-switch, the combinations of which means with the said apparatus are further features of the invention.

35 The apparatus may include a branch-conduit effective to pass a recycle stream of exhaust gas to the engine inlet. Such a branch-conduit ensures adequate nitrogen oxides removal capacity in the event of un-

usually high emissions or a design requirement for low-volume catalytic reactors.

65 The invention provides also an engine in combination with the apparatus, especially having internally-insulated exhaust ports; and also a reactor, preferably in the form of a modified exhaust manifold, adapted for insertion into the apparatus and containing the fibrous catalyst. The gases from other burners, for example from the burning of fuel oils, may also be advantageously treated to reduce their pollutant content. A further application of the invention resides in the removal of nitrogen oxides from the waste gases of nitric acid plants; addition of a combustible gas, for example a hydrocarbon, is necessary in this case to ensure non-oxidising conditions. In general, the waste gases will contain any gases required for the desired reactions to take place, for example steam or water-vapour and for the necessary non-oxidising conditions to be maintained, but if additional amounts of these are required they can be injected into the gas stream in the catalyst zone or, preferably, into the gas stream before it enters the catalyst zone and the devices of our invention can be adapted accordingly.

70 The conditions of contact of the gases with the catalyst may be chosen by simple trial, having due regard for the particular gases and the particular conditions of use. It may not be essential to eliminate the pollutants entirely, but the use of one or more of the devices described above can enable the emissions from, for example, automobile exhausts to be reduced considerably.

75 The invention is illustrated, but not limited, by the following Examples.

Example 1.

80 A sample of polycrystalline zirconia fibres containing 7% yttrium oxide and 7% nickel oxide was prepared from an aqueous precursor solution containing the mixed chlorides and acetates of the metals by the method disclosed in UK patent specification No. 1,360,197. The fibres had a mean diameter of 2 microns and had been fired at 1000° C. The fibres, in the form of a soft mat were reduced in a stream of H₂/5N₂ at 650° C. for 15 minutes after which they had turned black. X-ray diffraction showed the presence of a tetragonal zirconia, nickel metal, and traces of nickel oxide. The surface area as measured by nitrogen adsorption was 7 m²/gm. Approximately 1 gram of the mat was packed into a reactor at a bulk density of approximately 0.2 gm/cc. A gas simulating the exhaust from an internal combustion engine was passed through a 750° C. at a volume hourly space velocity of approximately 100000 hr⁻¹. The inlet and outlet gases had the following compositions:

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	ppm			% by weight	
	NO _x	NH ₃	CO	H ₂	O ₂
inlet	1781	—	2.8	3.0	1.0
outlet	521	200	2.3	2.0	under 0.1

Despite the high space velocity and small weight of catalyst, some 70% of the NO_x had been removed. At a higher temperature the conversion of NO_x would be more complete and less ammonia would be formed.

Example 2.

A sample of polycrystalline zirconia fibres in the cubic phase containing 10% alumina and 3% of cobalt metal in the form of the oxide was prepared from an aqueous precursor solution of the mixed chlorides and acetates of the metals, according to the method disclosed in UK patent specification No. 1,360,197; the 'green' or unfired fibres were first heated to 200° C. for 15 minutes followed by 10 minutes at 1000° C. After this they were sky-blue in colour. The fibres were reduced at 650° C. in a mixture of H₂/N₂ gases to give a black soft flexible mat. The fibres were of diameters in the range 1 to 3 microns.

The reduced mat was rolled up like a 'swiss-roll' and 0.85 gm of the reduced mat was introduced into the reactor through which simulated automobile exhaust gas could be passed. A simulated exhaust gas containing 1830 ppm hydrocarbons (as C₃), 2.5% CO, 2.5% H₂, 0.9% O₂, and 2350 ppm of nitrogen oxide, was passed through the catalyst bed at a rate of 300 litres per hour (space velocity about 70000 hr⁻¹). The inlet nitrogen oxides concentration of 2350 ppm was reduced to 20 ppm, and only 111 ppm of ammonia was formed. The percentage of nitrogen oxides removed was 99% despite the high space velocity and small weight of fibre used. After the test the fibres were discharged and found to be apparently unchanged in form.

Example 3.

A fibrous pad of zirconia fibres in the cubic phase with a mean diameter of 6 microns was soaked in a methanolic solution of cobalt nitrate (5% w/w) and thoroughly drained. The fibrous pad after firing at 500° C. had

gained in weight by 6%. A sample of this fibre was introduced into the test reactor in a gas stream similar to Example 2, but containing 3991 ppm nitrogen oxides, and at a temperature of 770° C. 40% of the nitrogen oxides in the inlet gas were removed.

Example 4.

100g of a fibrous catalyst based on stabilized zirconia and containing nickel catalyst promoted by barium (3% Ni and 1% Ba) was prepared in the form of long uniform strips of randomly oriented fibre. The strips had a width of 5 cm, a thickness of approximately 0.5 cm and a bulk density of up to 0.05g cm⁻³.

The strips of fibre were wound uniformly onto a cylindrical former, 10 cm diameter and 20 cm long, made from a sheet of heat-resisting nickel alloy, 0.07 cm thick and perforated with 0.2 cm diameter circular holes to give an open area of 40%. The fibre wrapping was compressed to give a layer thickness of 0.5 cm, covered by another perforated sheet and welded to give a device consisting of two concentric cylinders of perforated metal with a 0.5 cm layer of compressed fibre between them.

This device was mounted in a thermally-insulated container in the exhaust system of a 4-cylinder gasoline-powered internal combustion engine of 1600 cc capacity mounted in a dynamometer test-bed. The device was placed at a point just below the exhaust manifold in such a way that the exhaust gas flowed from the exhaust manifold, into the central area of the device, through the fibrous catalyst into the device container and out through the test-bed exhaust system. The system was sealed so that no air could enter at any point between the engine and the fibrous catalyst whilst the engine was running. The engine was run with nominally lead-free gasoline.

This apparatus was used to obtain the results given in Table 1.

TABLE 1

Engine Speed rpm	Brake Mean Effective Pressure bar	Catalyst Bed Temperature °C	Pressure Drop Across Catalyst Bed mbar	Exhaust Gas Analysis		
				Upstream CO % w/w	Upstream NO ppm by weight	Downstream NO ppm by weight
2000	1.75	500	33	3.9	500	400
3000	2.7	620	82	3.9	1200	450
4000	5.4	735	300	4.1	1400	600
TABLE 2						
3000	2.2	600	303	5.0	500	200
3000	2.2	620	298	3.1	1000	300
3000	2.1	640	298	1.5	1400	550
3000	2.1	650	300	0.8	1550	1100
4000	3.0	740	610	3.0	1500	300

ppm = parts per million

Example 5.

65g of a fibrous catalyst based on alumina, containing 0.1% ruthenium metal, were mounted in the same way as described in Example 4. The device was tested in a similar manner as described in Example 4 except that a 2-litre engine was mounted in the test-bed dynamometer.

The results obtained are given in Table 2.

Example 6.

Preparation of Fibrous Catalyst.

Zirconia and alumina fibres were prepared as described in U.K. patent specification No. 1,360,197. Thus various solutions of polymeric basic zirconium or aluminium salts were prepared which contained stabilisers, salts of catalytic metals and minor proportions of organic polymers such as high-molecular

weight poly(vinyl alcohol), polyethylene oxide and polyvinyl pyrrolidone. The solutions were adjusted to the viscosity required for spinning by the extrusion/air attenuation method, which was generally in the range 5—20 poise, and unfired fibres were collected on wire gauze or moving belts. These fibres were dried at

100—150° C., and fired at temperatures up to 1000° C. to give essentially shot-free fibres with diameters in the range 1—4 microns in the form of soft flexible blankets.

Zirconia-based fibrous catalyst, as used in test runs 1 to 29 (Table 4) were prepared from the following components:

1. Basic Zirconium Acetate Solution. 22% w/w ZrO_2
Ex Magnesium Electron Limited
2. Rare Earth Chloride Solution
Rare Earth Oxide Powder
Rare Earth Nitrate Solution
Yttrium Solution
as shown in Table 4
Ex Thorium Limited
3. Polyethylene Oxide Powder. MW 300,000
Ex Union Carbide Corporation
4. Analytical reagent quality transition metal chlorides
Chloroplatinic Acid
Ruthenium Chloride
Ex British Drug Houses Limited

The rare earth oxides, and chlorides derived from them, consisted of a grade containing 60% yttria. Sufficient rare earth or yttria salts or oxides dissolved in a small excess of hydrochloric acid were mixed with the zirconium acetate solution such that the rare earth oxide content was 7% by weight of the zirconia content, so that the final fired fibres were stabilised in the tetragonal form. The solutions were mixed with a solution of polyethylene oxide to give an organic polymer level of 2% by weight of the zirconia content, and the solutions were evaporated to give a viscosity of approximately 10 poise. The salts of the catalytic elements, in the form of chlorides or nitrides were co-dissolved either before or after evaporation to give the required concentration of catalyst in the fibres as detailed in Table 4. Alternatively similar solutions could be obtained by direct dissolution of zirconium carbonate, ex Magnesium Electron Limited, in glacial acetic acid, and with co-dissolution of the other components as solids. The fibres were dried at 100—150° C., charred at 350° C. and fired at 900° C. for 15 minutes to half-an-hour. Some samples were fired directly at 800° C., followed by 900° C. Fibrous catalysts containing cobalt or nickel were subsequently reduced in a 1:5 mixture of hydrogen and nitrogen at 700° C. to give black fibres containing some reduced metal from which a substantial proportion of the sulphur (present in the original zir-

conium acetate as sulphate impurity) had been removed in the form of hydrogen sulphide. The zirconia fibres exemplified had surface areas in the range 0.5—40 m²/g before use, which in general dropped to 0.5—20 m²/g after thermal cycling over several weeks at temperatures up to 900° C. in synthetic exhaust gases. The crystallite size of the tetragonal zirconia measured by X-ray diffraction was in the range 200—600 Å. Bore volume was in the range 0.01 to 0.06 cc/g.

Alumina-based fibrous catalysts were prepared from solutions of aluminium oxychloride having an Al:Cl ratio of approximately 2:1. The oxychloride solution was made by dissolving aluminium metal in hydrochloric acid with evolution of hydrogen. The resultant solution was mixed with catalytic salts to give the compositions indicated in Table 4, and sufficient polyvinyl-alcohol, or polyvinyl pyrrolidone were co-dissolved to give a polymer level of 6% by weight of the equivalent alumina content. The solutions were adjusted to a viscosity of 20 poise and spun by the extrusion/air-attenuation method to give fibres with a mean diameter of 3 microns. The fibres were briefly dried, and passed into a furnace containing a steam atmosphere at 350° C. After 15 minutes at 350° C. the fibres were fired in air at 900° C. for 15 minutes to give strong flexible fibres. Surface areas of the alumina fibres were in the range 5—150 m²/g, generally after use in the range

40—70 m²/g, with pore volumes of 0.01 to 0.07 cc/g. X-ray diffraction showed that the fibres as formed at 800° C. were essentially amorphous, but that the alumina pattern, with traces of chi-alumina developed slowly with time at 600—800° C. or rapidly at 900° C., giving apparent mean crystallite sizes in the range 50—200Å.

Feed Gases

The fibrous catalysts were tested using

synthetic exhaust gas mixtures comprising nitric oxide, carbon monoxide, hydrogen, methane, toluene, oxygen, nitrogen and steam. The catalysts were examined under two gas compositions to correspond to air-fuel ratios (A/F ratios) 13 and 14. The two A/F ratios used are defined in Table 4. Variations in the feed rate around the nominal desired value were recorded throughout a test run and the ranges observed for the different gases are shown in Table 3.

TABLE 3
Air-fuel ratio = 13.

Component	Nominal Concentration (v/v)	Range (v/v)
NO	1000 ppm	900—1200 ppm
CO	3%	3—3.6%
H ₂	1.2%	1—2%
CH ₄	700 ppm	500—750 ppm
C ₇ H ₈	250 ppm	200—500 ppm
O ₂	0.25%	0.2—0.45%
H ₂ O	13%	10—15%
N ₂	balance	balance

Air-fuel ratio = 14

Air-fuel ratio = 14

Component	Nominal Concentration (v/v)	Range (v/v)
NO	2000 ppm	1800—2400 ppm
CO	2.0%	2.0—2.3%
H ₂	0.7%	0.35—0.75%
CH ₄	600 ppm	400—600 ppm *
C ₇ H ₈	200 ppm	200—500 ppm
O ₂	0.25%	0.15—0.45%
H ₂ O	13%	10—15%
N ₂	balance	balance

* In some cases CH₄ was not used.

Apparatus

The test apparatus consisted of conventional integral through-flow reactors. Analysis was primarily by gas chromatography. Nitric oxide concentrations were measured by a chemiluminescence analyser except in the cases where a Non-Dispersive Infra-Red Analyser was used. Neither instrument showed any

significant sensitivity to ammonia under the analysis condition and was therefore not subject to error due to the presence of ammonia in the gas stream.

10

Nitric Oxide Conversion

The percentage NO conversion is defined by the expression:—

15

$$\text{Percentage NO conversion} = \frac{([\text{NO}]_{\text{feed}} - [\text{NO}]_{\text{exit}}) \times 100}{[\text{NO}]_{\text{feed}}}$$

where [NO] is the concentration of NO in the gas stream.

Ammonia Selectivities

The selectivity of the catalyst for producing ammonia is quoted where the results are available and is defined as

20

$$\text{Ammonia selectivity} = \frac{[\text{NH}_3]_{\text{exit}} \times 100}{[\text{NO}]_{\text{feed}} - [\text{NO}]_{\text{Exit}}}$$

Bed packing

- 25 The fibres were either packed into the reactors in the form of a highly-compressed pad indicated by * in Table 4, or they were slurried in water either with or without a diluent fibre. In the latter case the fibres were mixed together with water in a liquidizer, which was operated for 60 to 120 seconds. The slurry was then added to the reactor and the water sucked off to compact the pad.

Space velocity

The gas hourly space velocity (GHSV) is defined as the volume of gas measured at standard temperature and pressure which passes through unit volume of the fibrous catalyst present in the bed, during 1 hour. The diluent fibre and fibrous catalyst are assumed to have the same packing density.

35

40

TABLE 4
TEST RESULTS

Run No.	Nominal Composition of Fibrous Catalyst (wt % of catalytic agent based on last named component.	Surface Area after Use ($\text{m}^2 \text{g}^{-1}$)	Weight of Catalytic Fibre (g)	Weight of Diluent Fibre (g)	Bed Density (g.cm^{-3})	GHSV (hr^{-1})	NO_x Conv. (%)	Net CO Conv. (%)	Hydrocarbon conv. (%)	Reaction Temp. ($^{\circ}\text{C}$)	A/F Ratio	Ammonia Selectivity % at ($^{\circ}\text{C}$)
1	3% Co/ Y_2O_3 / ZrO_2	0.6	2.000	NIL	0.30	32,600	80	4	50	857	13	—
2	3% Co/ Y_2O_3 / ZrO_2	3.2	0.744*	NIL	0.11	30,600	30	5	70	820	13	—
3	3% Co/1% Cu/REO/ ZrO_2	1.6	3.00	NIL	0.28	20,580	62	30	—	700	13	—
4	3% Co/1/2% Mn/REC/ ZrO_2	1.9	1.854*	NIL	0.14	16,560	90	12	1	750	13	—
5	0.5% Co/5 CuO/REO/ ZrO_2	1.0	3.881*	NIL	0.29	16,560	90	3	70	700	13	—
6	3% Co/1% Cr/REO/ ZrO_2	4.0	2.789*	NIL	0.13	9,940	76	40	65	750	13	—
7	3% Ni/REC/ ZrO_2	0.5	1.455*	NIL	0.17	35,000	77	3	38	645	13	—
8	3% Ni/1% Ba/ Y_2O_3 / ZrO_2	0.5	0.500	3.5	0.27	116,230	90	3	9	670	13	39 478+
9	3% Ni/1% Cu/REN/ ZrO_2	4.0	4.000	NIL	0.26	14,200	91	30	50	550	14	25 800
10	2% CuO/2% V_2O_5 /REO/ ZrO_2	2.4	3.000	NIL	0.29	21,600	90	5	—	650	13	—
11	2% Cu/2% Mn/REN/ ZrO_2	—	2.286	NIL	0.15	14,500	90	70	60	680	14	84 530
12	3% Cu/REC/ ZrO_2	4.4	4.000	NIL	0.20	10,660	95	40	—	550	14	65 500

TABLE 4 (continued)
TEST RESULTS

Run No.	Nominal Composition of Fibrous Catalyst (wt % of catalytic agent based on last named component.)	Surface Area After Use (m^2g^{-1})	Weight of Catalytic Fibre (g)	Weight of Diluent Fibre (g)	Bed Density ($\text{g}\cdot\text{cm}^{-3}$)	GHSV (hr^{-1})	NO_x Conv. (%)	Net CO Conv. (%)	Hydrocarbon conv. (%)	Reaction Temp. ($^{\circ}\text{C}$)	A/F Ratio	Ammonia Selectivity % at ($^{\circ}\text{C}$)
13	0.5% Ru/REO/ ZrO_2	8.8	4.000	NIL	0.21	11,500	95	20	30	420	14	2.5 495
14	1% Pd/REO/ ZrO_2	6.8	4.000	NIL	0.23	12,500	90	19	97	710	14	≥ 75 495
15	0.01% Ru/REO/ ZrO_2	4.7	4.000	NIL	0.20	10,940	96	9	50	542	13	6 -
16	3% Ni/1% Cu/0.1% Ru/REO/ ZrO_2	4.1	4.000	NIL	0.24	12,960	93	33	38	500	14	3.8 490
17	0.1% Ru/10% Al_2O_3 /REO/ ZrO_2	-	0.820	3.23	0.20	49,990	95	23	25	550	14	12 496
18	0.1% Ru/REO/ ZrO_2	-	1.010	3.12	0.19	39,390	90	26	30	550	14	12 535
19	0.1% Ru/5% Al_2O_3 /REO/ ZrO_2	-	0.980	3.00	0.17	38,360	98	22	19	550	14	6 515
20	0.1% Ru/2% Ni/REO/ ZrO_2	-	0.400	3.600	0.23	121,920	70	7	9	600	13	14 665
21	0.1% Rh/REO/ ZrO_2	-	0.430	3.638	0.20	99,910	91	17	65	550	14	45 520
22	0.1% Ru/3% Cu/REO/ ZrO_2	-	0.400	3.600	0.20	106,830	93	13	10	550	13	33 495
23	3% Fe/REC/ ZrO_2	2.2	1.465*	NIL	0.21	37,000	98	4	28	500	13	33 500+
24	3% Fe/1% Co/REC/ ZrO_2	0.5	2.862*	NIL	0.14	9,983	90	48	28	850	13	61 900

TABLE 4 (continued)
TEST RESULTS

Run No.	Nominal Composition of Fibrous Catalyst (wt % of catalyst agent based on last named component)	Surface Area After Use (m^2g^{-1})	Weight of Catalytic Fibre (g)	Weight of Diluent Fibre (g)	Bed Density ($\text{g}\cdot\text{cm}^{-3}$)	GHSV (hr^{-1})	NO_x Conv. (%)	Net CO Conv. (%)	Hydrocarbon conv. (%)	Reaction Temp. ($^{\circ}\text{C}$)	A/F Ratio	Ammonia Selectivity % at ($^{\circ}\text{C}$)
25	3% Fe/Cu/REC/ZrO ₂	0.8	3.128*	NIL	0.14	9,630	84	23	—	800	13	51 900
26	3% Fe/1% Cr/REC/ZO ₂	2.5	3.220*	NIL	0.15	10,170	90	53	—	760	13	81 620
27	6% Fe/REC/ZrO ₂	1.9	4.00	NIL	0.24	12,980	94	39	—	460	13	90 500
28	3% Fe/1% Mo/REC/ZrO ₂	2.6	4.00	NIL	0.20	10,950	95	19	—	550	13	70 500
29	3% Fe/CaO/5% Al ₂ O ₃ /ZrO ₂	1.4	4.00	NIL	0.20	10,730	92	49	25	700	13	90 500
30	0.5% Ru/Al ₂ O ₃	57.6	0.310	3.690	0.23	160,000	99	35	10	400	14	6 515
31	0.1% Ru/Al ₂ O ₃	60.0	0.200	3.800	0.30	140,000	95	20	—	600	14	0.6 480
32	6% Ni/Al ₂ O ₃	—	0.500	3.500	0.35	149,000	90	4	20	650	13	—
33	0.1% Ru/3% Cu/Al ₂ O ₃	—	0.120	3.900	0.35	616,790	65	17	42	684	14	5 715
34	0.1% Ru/3% Ni/Al ₂ O ₃	—	0.120	3.900	0.23	403,060	60	0	64	690	14	2 695
35	0.1% Ir/Al ₂ O ₃	—	0.120	3.900	0.25	471,420	55	4	59	700	14	>60 700

* denotes fibre packed as a pad

REC denotes Rare Earth Chlorides

REO denotes Rare Earth Oxides

REN denotes Rare Earth Nitrates

+ NDIR analyser used for NO analysis

WHAT WE CLAIM IS:—

1. A method for reducing the quantity of carbon monoxide, hydrocarbons or nitrogen oxides in gases which comprises contacting the said gases under substantially non-oxidising conditions (as herein defined) with a fibrous catalyst comprising a synthetic refractory fibre and a catalytic agent which promotes one or more reactions by which at least one of the said components is wholly or partly destroyed.
2. A method according to Claim 1 in which the gases are contacted with the fibrous catalyst at a temperature of at least 400° C.
3. A method according to Claim 2 in which the temperature is from 600° C. to 1000° C.
4. A method for treating an internal combustion engine exhaust gas having a start-up phase and a running phase, the running phase being operated according to a method as claimed in any one of the preceding claims, and the start-up phase being operated prior to the running phase under oxidising conditions with added air in the presence of the fibrous catalyst until the operating temperature of the fibrous catalyst has been reached.
5. A method according to any one of the preceding claims in combination with a subsequent oxidation stage and/or further reaction over a carbon monoxide shift or methanation catalyst.
6. A method according to Claim 4 in combination with a subsequent oxidation stage and having an air supply upstream of the fibrous catalyst during the start-up phase and between the fibrous catalyst and the oxidation catalyst during the running phase.
7. A method according to any one of the preceding claims wherein the synthetic refractory fibre is an inorganic oxide.
8. A method according to Claim 7 wherein the inorganic oxide comprises one or more of the oxides alumina, zirconia, titania or silica.
9. A method as claimed in Claim 7 or 8 wherein the refractory fibre is prepared as disclosed in United Kingdom Patent Specification No. 1,360,197.
10. A method as claimed in any one of the preceding claims wherein the refractory fibre has an average diameter less than 20 microns.
11. A method as claimed in Claim 10 wherein the refractory fibre has an average diameter in the range 0.5 to 5 microns.
12. A method as claimed in any one of the preceding claims wherein the surface area of the fibrous catalyst is greater than 0.5 square metres per gram.
13. A method as claimed in Claim 12 wherein the surface area of the fibrous catalyst is from 5 to 150 square metres per gram.
14. A method as claimed in any one of the preceding claims wherein the catalytic agent is a metal of Group VIII of the Periodic Table or a mixture of two or more of the said metals.
15. A method as claimed in Claim 14 wherein the metal is ruthenium, iridium, rhodium, iron, nickel or cobalt.
16. A method as claimed in any one of the preceding claims for treating an internal combustion engine exhaust gas in which the engine fuel contains 200—1000 parts per million by weight of sulphur and the catalytic agent of the fibrous catalyst is cobalt.
17. A method as claimed in any one of the preceding claims wherein the proportion of catalytic agent in the fibrous catalyst is 0.001 to 10% by weight.
18. A method as claimed in Claim 15 wherein the ruthenium, iridium or rhodium is present in the fibrous catalyst at a concentration of 0.001 to 1% by weight calculated as the metal.
19. A method as claimed in Claim 15 wherein the nickel or cobalt is present in the fibrous catalyst at a concentration of 1 to 10% by weight calculated as equivalent NiO.
20. A combination method according to any one of Claims 5 and 6 to 19 insofar as they depend on Claim 5 in which the subsequent oxidation stage is carried out with an oxidation catalyst comprising a platinum group metal in a concentration of 0.002 to 1.0% on a refractory support.
21. A combination method according to any one of Claims 5 and 6 to 19 insofar as they depend on Claim 5 in which the subsequent oxidation stage is carried out with an oxidation catalyst comprising the oxide of one or more base metals from Group VIII of the Periodic Table and an oxide of chromium or tungsten.
22. A method as claimed in any one of Claims 1 to 19 in which the catalytic agent is incorporated in the refractory fibre by dispersing or dissolving the catalytic agent or its precursor in a fibrising composition from which the refractory fibre is made.
23. A method as claimed in Claim 22 in which the catalytic agent is dispersed or dissolved in an aqueous solution of an aluminium or zirconium compound suitable for fibrising.
24. A method according to Claim 1 substantially as described and as set forth in any of Examples 1 to 3.
25. A method according to Claim 1 substantially as described and as set forth in any of Examples 4 to 6.
26. Reactor suitable for carrying out a method according to any one of the preceding claims comprising a chamber adapted to hold the fibrous catalyst as a removable pre-formed unit and means to conduct a stream of gas into contact with the fibrous catalyst.
27. Apparatus suitable for treating an internal combustion engine exhaust gas by a

- method according to any one of Claims 1 to 25 which comprises an insulated first reactor as claimed in Claim 26 adapted to be mounted close to an internal combustion engine and to be fed from the engine exhaust port or ports, a second reactor disposed downstream of the first reactor and an inlet means adapted to feed alternatively at or before the insulated reactor and between the reactors.
- 5 28. Apparatus according to Claim 27 including a branch conduit effective to pass a recycle stream of exhaust gases to the engine inlet.
- 10 29. An internal combustion engine in combination with an apparatus according to Claim 27 or 28.
30. An engine according to Claim 29 having internally insulated exhaust ports.
31. A catalyst unit comprising a pre-formed mass of fibrous catalyst comprising a synthetic refractory fibre and a catalytic agent, which unit is suitably shaped for introduction into a reactor according to Claim 26 or an apparatus according to Claim 27 or 28.
- 20 32. A catalyst unit according to Claim 31 contained within a cage made of metal gauze or expanded metal.
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